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SURFACE-SULPHONATED POLYSTYRENE AS A CANDIDATE MATERIAL FOR RESPIRATOR EYEPIECES

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Surface-Sulphonated Polystyrene as a Candidate Material for Respirator Eyepieces

by

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(with an appendix by D.K. Hale, Chemical Research Laboratory, Teddington)

Introduction

During a discussion of anti-dimming problems it was suggested ([redacted] that many of the difficulties associated with the use of a soluble spreading agent on the glass eyepieces of respirators might be avoided by utilizing the hydrophilic properties of surface-sulphonated polystyrene. Experience indicated that the material could be prepared by relatively simple means and that it successfully resisted misting under light condensation conditions.* It remained to determine (a) whether such a surface could deal adequately with the much greater volume of condensate which occurs in a respirator during wear and (b) what method of preparation was required to give a product of uniform quality. It was envisaged that the material could be used as a thin sheet attached to the existing glass eyepiece or as a thicker disc to replace the glass completely.

Arrangements were made for the method of preparation to be investigated at the Chemical Research Laboratory, Teddington, where considerable experience in the preparation of sulphonated polystyrene in another connection was already available. At various stages during the work, samples were sent to C.D.E.E. for practical evaluation.

All samples examined failed to reach an acceptable standard of anti-dimming performance and, as there appears to be no prospect of further improvement, the investigation has been discontinued.

Experimental Method

Details of the method of preparation of the material and of the preliminary tests applied to it at C.R.L. are given in an appendix to this report.

Five batches of samples were received from C.R.L. in the form of discs 2" or $2\frac{1}{2}$" in diameter and 1/24" to $\frac{1}{8}$" thick. Some very thin sheets, which were attached to glass discs for testing, were included in the second batch.

Footnote. *Surface-sulphonated polystyrene has been used successfully for the front window of diving helmets, but the conditions of use in that instance differ from those in a respirator in that the polystyrene is completely wetted, often by immersion, before use.

With the exception of the last batch, which was of Transpex, the optical quality of the samples was generally poor, but this did not appreciably affect their assessment since allowance could be made for most of the defects.

Assessment of performance was based in the first instance on the optical quality of the film of water which formed on the disc when it was exposed to condensation in a modified form of the apparatus described in P.T.P. 271. This consisted of a chamber containing saturated air at 35°C., into which could be inserted two cylindrical water-cooled cells, one plane (vertical) end of each cell being formed from one of the discs under test. An illuminated sheet of graph paper placed a short distance behind each cell formed the test object for estimating the interference with vision through the disc produced by any irregularities in the water film. Condensation was at the rate of 0.3 to 1.1 c.c./hr. according to experimental conditions.

All discs were given their first exposure to condensation in the condition in which they were received from C.R.L. In subsequent tests they were swabbed with a fine linen cloth dipped in distilled water immediately before use and dried in air at room temperature. The drying was [illegible] because this is the condition in which they would normally be used in the field.

A few of the discs were fitted in place of the glass eyepiece of a Light Type respirator and worn at room temperature and in a cold chamber just below the freezing point.

Performance

All five batches of samples gave essentially the same performance and the description which follows is typical of the whole series.

Immediately on exposure to condensation, nearly all the discs showed some degree of misting, varying from slight to heavy according to the disc used and the rate of condensation, but later, as condensate accumulated, all the discs developed discrete droplets of low contact angle. These droplets continued to grow and coalesce for some time, but the process did not go to completion and the film stabilized as soon as sufficient contact had been made between the droplets to drain away the condensate as rapidly as it formed. The resulting film was heavily marked by dimples and furrows formed between the uncoalesced droplets. Occasionally small areas of flat film were formed, but more generally the imperfections were not separated by more than one or two millimetres, and considerable interference with vision through the disc was accordingly experienced. The practical effect of this wrinkling was such that when the discs were worn in the respirator, print which could normally be read at a distance of 5 feet had to be brought up within 12 inches before it could be discerned after 30 minutes' wear.

A slight improvement in performance was obtained when the discs were swabbed with a linen cloth dipped in distilled water immediately before test and given only sufficient drying to remove visible traces of water. A total exposure to condensation amounting to 8-10 hours, interspersed with frequent intervals for drying, produced no sensible change in performance, but 24 hours' immersion in distilled water (or, at C.R.L., 24 hours' continuous exposure to saturated air) largely destroyed the hydrophilic nature of the surface.

If the discs were given a thin coating of anti-dim compound before exposure or if the water film were mechanically smoothed out by sweeping the disc with the wet edge of a piece of filter paper, a uniform and stable film of good optical quality was obtained even with discs of the poorest performance. Equally satisfactory results were obtained when the anti-dim compound was replaced by a film formed from the sodium salt of polystyrene sulphonic acid, obtained by spreading a small quantity of solution over the disc and evaporating to dryness.

A few rough measurements of the contact angle with the Transpex surfaces were made by forming small bubbles of air beneath a disc placed horizontally in a trough of water. The bubbles readily displaced the water from the surface and an appreciable equilibrium angle of contact of about 22° was formed at the boundary. Similar measurements with un-treated polystyrene gave a value of 72°. Although sulphonation had thus considerably reduced the angle of contact, spontaneous spreading of the condensate over the surface could not be expected in the light of these measurements.

Since the optical quality of the water films was so poor and clearly a good deal below the minimum standard acceptable, very little work was done to investigate the suitability of the sulphonated surface in other respects. A brief investigation showed that the discs were particularly resistant to oil contamination. Even after prolonged contact, the oil could be readily removed by rubbing with a damp cloth or floated off by condensation. The surface was, also, reasonably resistant to abrasion during cleaning, some 70% of the area surviving 3000 rubs with a damp linen cloth at a pressure of $1\frac{1}{2}$ lb/in^2.

Discussion

From the earlier experiments it was suspected that the irregular character of the water film might arise from insufficient or uneven sulphonation of the surface. In the succeeding samples, therefore, the sulphonation was increased to the maximum practicable (i.e. just short of rendering the surface soluble) and proved to be uniform by the methylene blue test (see appendix). As no improvement in the quality of the condensed water film was obtained, it must be concluded that neither of these factors was responsible for the failure. The final batch (Transpex) showed that minor imperfections of the surface had also played no part.

The satisfactory performance obtained with coatings of the acid may have been due to the higher degree of sulphonation obtained in that way, but more probably arose from the soluble nature of the coating.

The investigation has not been exhaustive, but has been sufficient to show that the use of sulphonated polystyrene will not dispense with the need for a soluble spreading agent on the eyepiece. Sulphonated polystyrene therefore presents no advantage over glass as a material for respirator eyepieces in current equipment, but where the choice of material is limited to a plastic by reason of the shape of eyepiece or other considerations, the use of a sulphonated surface has much to recommend it since its performance, in conjunction with an anti-dimming compound, is undoubtedly superior to that of the untreated material (or of perspex) used in the same manner.

Conclusions

1. If sulphonation is kept below the level at which the surface itself becomes soluble, the condensate does not spread over the surface to form a uniform film without the aid of a spreading agent.

2. The uneven film of condensate formed in the absence of a spreading agent gives rise to an unacceptably high degree of interference with vision through the film.

3. The use of surface-sulphonated polystyrene does not, therefore, offer any opportunity of dispensing with a soluble anti-dimming agent in current types of service equipment.

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The laboratory work described above was carried out by Mrs. B.H. Harvey.

KPS/JB

Appendix to P.T.P. 353

Preparation of surface sulphonated polystyrene sheet

The treatment of polystyrene sheet by surface-sulphonation to prevent "misting" in humid atmospheres has been described in the patent literature (British Patent 572, 985, 1945) and the preparation of materials of this type was investigated.

A number of sulphonation procedures have been examined. The use of a liquid sulphonating agent has recently been described by Westermark (Acta Chem. Scand. 6, 1194, 1952). In our work however, liquid sulphonating agents were found to lead to uneven films of sulphonated material and treatment with sulphur trioxide vapour was found to be very much more satisfactory.

Preliminary experiments were carried out with discs (2" diam.) of moulded polystyrene. These were exposed to the vapour of 60% oleum at room temperature for varying times, washed with water, dilute sodium hydroxide (0.5%) and water. The degree of sulphonation was assessed by treating the discs with methylene blue solution (0.128 grams per litre) for 10 minutes, washing with water and determining the optical density using a Spekker absorptiometer. The results indicated that the highest degree of sulphonation was obtained with a time of exposure of about 1 minute. With longer periods of exposure, the sulphonated layer apparently became detached from the polystyrene on washing.

The anti-dimming properties of the treated surfaces were tested by placing the sheet over the mouth of a boiling tube containing water at 40°C. With untreated polystyrene or glass a mist is formed in 5 to 15 seconds. After longer periods of exposure, small droplets of water are formed. With a glass surface treated with "anti-dimming" compound, no mist or droplet formation is observed; a continuous film of liquid is formed on the treated surface.

Early samples prepared as described above were found to possess poor anti-dimming properties but a marked improvement was obtained if the surface was thoroughly cleaned before sulphonation. Treatment with chromic acid (10 g. potassium dichromate, 400 ml water, 400 ml conc. sulphuric acid) at 60° for 15 minutes was found to be necessary.

When tested immediately after preparation the surface-sulphonated discs showed similar behaviour to that of glass treated with anti-dim compound. Some deterioration in anti-dimming behaviour was observed after exposure of the sulphonated surfaces to the laboratory atmosphere overnight or on heating at 50°C for 20 minutes. The original behaviour (i.e., no mist and a continuous liquid film) was however restored by light rubbing with a clean damp cloth. Rather surprisingly, this simple treatment proved effective in restoring a surface which had been heavily contaminated with vaseline.

The method of surface-sulphonation described was found to give similar results with polystyrene from different sources in the form of moulded discs, cast sheet and thin films.

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